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#### EUROPEAN PATENT APPLICATION

2:) Application number: 91106475.6

② Date of filing: 15.04.88

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- © Publication number of the earlier application in accordance with Art.76 EPC: 0 291 179
- Designated Contracting States:

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- Inventor: Suh, Kyung W. 1533 Welsh Hills Road Granville, Ohio 43023(GB)
- Representative: Burford, Anthony Frederick et al W.H. Beck, Greener & Co. 7 Stone Buildings Lincoln's Inn London WC2A 3SZ(GB)
- Preparation of polymer foam and product.
- (57) A method for producing a thermoplastic polymer extruded foam body having an average cell size of from 0.05 mm to 3.5 mm, a density of from 1.0 lbs/ft3 (16 kg/m3) to 5.0 lbs/ft3 (80 kg/cm3), a minimal cross- sectional thickness of 0.5 in (1.3 cm) and a minimal cross-sectional area of 8 in2 (52 cm2) comprises the steps of: heat plastifying the resin; introducing the plastified resin into a mixing device; introducing a blowing agent into the mixing device; maintaining a pressure in the mixing device at or above a pressure greater than an equilibrium vapor pressure of the blowing agent in the resin and blowing agent mixture: passing the mixture through a cooling device; passing the mixture through a die having a given die pressure greater than atmospheric pressure; maintaining a specific defined minimum critical pressure drop between the pressure at the inlet of the mixing device and the inlet of the die. Blowing agents useful in such process are disclosed as well polymer foam bodies made by the process and consistently having improved uniformity of surface quality.



#### **EUROPEAN SEARCH** REPORT

EP 91 10 6475

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Category		th indication, where appropriate. vant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CI.5)
X	US-A-4 222 729 (RAGAZZ	(INI ET AL)	1-4	B 29 C 67:22 C 08 J 9:12
Α		; figure 1 *** column 4, line 45 - nn 6, line 61 - line 68 *** column s 1 ***	7-11	C 08 J 9/14
X	DD-A-114 926 (LAUTERB	ERG)	1-4,10	-
Y	DD-A-114 926 () page 3, column 1, line 22	- line 38 * *	5-9,11-12	
Y	US-A-4 387 169 (ZABROC abstract; claims; examples	-	5-9,11	
Υ	EP-A-0 079 012 (MARYLA	ND CUP CORP)	11-12	
A	EP-A-0 079 012 () page 3. line 11 - line 30: c	taims 1-2,28-32; examples **	1-4,10	
Α	US-A-3 300 554 (BACHUS column 3, line 14 - line 16 7, line 21 - line 32 **	5) ; claims; figures 3B,7 *** column	1-3,11	TECHNICAL FIELDS SEARCHED (Int. C1.5)  B 29 C
A	US-A-4 071 591 (KOBAYA column 4, line 14 - line 61		1-4,11	
A	US-A-4 613 471 (HARRIS) column 7, line 63 - column	) n 8, line 39; claims 1-17; figure 1	. 1-12	
Α	US-A-3 972 970 (TAYLOR column 6. line 31 - column		1-2,11-12	
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	The present search report has t	peen drawn up for all claims		
	Place of search	Date of completion of search		Examiner
	The Hague	15 November 91		PIPPING L.E.L.

#### CATEGORY OF CITED DOCUMENTS

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- Y: particularly relevant if combined with another document of the same catagory
- A: technological background
  O: non-written disclosure
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- E: earlier patent document, but published on, or after the filing date
- D: document cited in the application
- L: document cited for other reasons
- &: member of the same patent family, corresponding document



Y: particularly relevant if combined with another

document of the same catagory

A: technological background

#### **EUROPEAN SEARCH** REPORT

Application Number

EP 91 10 6475

D	OCUMENTS CONSI	DERED TO BE RELE	VANT	
Category		n indication, where appropriate, vant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CI.5)
А	US-A-3 817 669 (BUCKNE claims; figure 2: examples		1-12	
	·			
				TECHNICAL FIELDS SEARCHED (Int. Cl.5)
				SEARCHED (III. Cl.s)
		· .		
	The present search report has	nago drawa un for all claims		2
		<u></u>		Examiner
	Place of search The Hague	Date of completion of search 15 November 91		PIPPING L.E.L.
X:	CATEGORY OF CITED DOC particularly relevant if taken alone particularly relevant if combined wi	•	arlier patent docum he filing date locument cited in th	ent. but published on. or after

L: document cited for other reasons



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**③** 

### EUROPEAN PATENT APPLICATION

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This application was filed on 23 - 04 - 1991 as a divisional application to the application mentioned under INID code 60.

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- (7) Applicant: THE DOW CHEMICAL COMPANY 2030 Dow Center Abbott Road Midland, MI 48640(US)
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- (74) Representative: Burford, Anthony Frederick et W.H. Beck, Greener & Co. 7 Stone Buildings Lincoln's Inn London WC2A 3SZ(GB)
- Preparation of polymer foam and product.
- (5) A method for producing a thermoplastic polymer extruded foam body having an average cell size of from 0.05 mm to 3.5 mm, a density of from 1.0 lbs/ft3 (16 kg/m3) to 5.0 lbs/ft3 (80 kg/cm3), a minimal cross-sectional thickness of 0.5 in (1.3 cm) and a minimal cross-sectional area of 8 in<sup>2</sup> (52 cm<sup>2</sup>) comprises the steps of heat plastifying the resin; introducing the plastified resin into a mixing device; introducing a blowing agent into the mixing device; maintaining a pressure in the mixing device at or above a pressure greater than an equilibrium vapor pressure of the blowing agent in the resin and blowing agent mixture; passing the mixture through a cooling device; passing the mixture through a die having a given die pressure greater than atmospheric pressure; maintaining a specific defined minimum critical pressure drop between the pressure at the inlet of the mixing device and the inlet of the die. Blowing agents useful in such process are disclosed as well polymer foam bodies made by the process and consistently having improved uniformity of surface quality.

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Such foam preparation is set forth in U.S. Patent Nos. 4.393.016 and 4.451.417. respectively. An alternative blowing agent system utilizing carbon dioxide and an alkane is set forth in U.S. Patent Nos. 4.344.710 and 4,424,287.

Alkenyl aromatic polymer foam has also been prepared as set forth in U.S. Patent No. 4,636,527, using as a blowing agent a mixture of carbon dioxide, ethyl chloride and optionally a fluorocarbon member selected from dichlorodifluoromethane, 1-chloro-1,1-difluoroethane and mixtures of these fluorocarbons.

It would be desirable if there were available a process for the preparation of alkenyl aromatic polymer foam which did not cause blow holes, poor skin quality and gassing at the die.

It would also be desirable if in the process of the present invention there was produced a novel alkenyl aromatic polymer foam prepared from more environmentally acceptable blowing agents.

These benefits and other advantages in accordance with the present invention are readily achieved in a process for producing an alkenyl aromatic synthetic resin extruded foam body having closed cells with an average cell size of from about 0.05 millimeter (mm) to about 3.5 mm, a density of from about 1.0 pound per cubic foot (pcf) (16kg/m³) to about 0.5 pcf (80kg/m³), a minimal cross-sectional thickness of one half (1.2) inch (1.3cm) and a minimal cross-sectional area of eight (8) square inches (52cm²) including the steps of; (a) heat plastifying the alkenyl aromatic synthetic resin; (b) introducing the plastified resin and a blowing agent into a mixing device having an inlet maintained at a pressure, P<sub>M</sub>, which is greater than an equilibrium vapor pressure of the blowing agent in the alkenyl aromatic synthetic resin and blowing agent mixture; (c) passing the mixture through a cooling device; (d) passing the cooled mixture through a die having a die inlet pressure, P<sub>D</sub>, which is greater than atmospheric pressure; all wherein the quality of the foam's surface is controlled by deliberately maintaining the pressure drop from the mixer's inlet to the die's inlet, ΔP, at a pressure drop greater than or equal to an empirically predetermined minimum and critical pressure drop, ΔP<sub>C</sub>, for the given mixture of resin and blowing agent.

Also contemplated within the scope of the present invention is an alkenyl aromatic synthetic resin extruded foam prepared from known blowing agents in accordance with the method of the present invention.

Further contemplated as within the scope of the present invention is an alkenyl aromatic synthetic resin extruded foam prepared from more environmentally acceptable blowing agents in accordance with the method of the present invention, which foams have good to excellent surface quality as measured by a test given hereinafter.

Still further contemplated within the scope of the present invention are polystyrene extruded foams prepared in accordance with the present invention.

Yet further contemplated within the scope of the present invention are styrene/acrylic acid copolymer extruded foams prepared in accordance with the present invention.

Still yet further contemplated within the scope of the present invention are ionomeric styrene acrylic acid copolymer extruded foams prepared in accordance with the present invention.

For decades prior to this invention was made, it had been believed that as long as a die pressure is maintained above a vapor pressure of blowing agent systems at a given foaming temperature, it is possible to produce good quality closed cell low density foams with a good skin quality. Commercial foams prepared from current methods sometimes contain different amounts of blow holes and skin cracks or textures. Furthermore, it is difficult to produce a low density extruded foam with blowing agent systems containing environmentally acceptable blowing agents such as methane, ethane, carbon dioxide, nitrogen, water, and certain fluorocarbons and chlorofluorocarbons containing hydrogen.

In marked contrast to the prior art, foams prepared in accordance with the present invention can "consistently" have a low density extruded foam with improved skin quality and physical properties. The present invention also reduces the scrap rate resulting in a better utilization of raw materials, cost savings, and less emission of volatile organic compounds to the atmosphere.

Figures 1-19 are self-explanatory schematic drawings of various processes according to the invention involving measurement of the pressure drop from the mixer's inlet to the die's inlet.

Also, in contrast to the prior art, the present invention provides an "early warning" signal of deterioration in extrusion conditions before the deterioration is so great that it actually causes blow holes in the surface of the final foam product in particular  $\Delta P$  can be easily measured instrumentally on a continuous basis and an alarm sounded if the value of  $\Delta P$  ever falls below a given value.

The following steps have been among those found to be effective in correcting for a drift downwards in the value of  $\Delta P$ . Firstly, the temperature of the mixing device can be reduced by a few degrees centigrade. Secondly, a throttle valve located between the mixer and the die can be partially closed. Thirdly, the blowing agent flow rate can be reduced, thereby increasing the viscosity of the partially mixed polymer and blowing agent flow rate of the polymer can be increased (as by increasing the RPM of a dear

ozcne depletion in the preparation of foam in accordance with the present invention and eliminate or reduce the concentration of fully halogenated chlorofluorocarbons include: ethyl chloride (EtCl), carbon dioxide ( $CO_2$ ), chlorodifluoromethane, 1,1-difluoroethane, nitrogen ( $N_2$ ), water ( $H_2O$ ), the aliphatic hydrocarbons including, methane, ethane, ethylene, propane, propylene, butane, butylene, isobutane, pentane, neocentane, isopentane, hexane, heptane and mixtures of any of these additional blowing agents.

Particularly useful are methane, ethane, propane, ethyl chloride, carbon dioxide, nitrogen, water and chlorodifluoromethane (CFC-22).

The term "blowing agent" as used in this specification shall refer to both a single blowing agent and mixtures of blowing agents.

The blowing agent usually is present in the process of the present invention at a level of about 3 to about 30 parts by weight per 100 parts by weight of alkenyl aromatic synthetic resin.

Specific blowing agents useful in the process of the present invention for the preparation of alkenyl aromatic synthetic resin foams are (all percents are weight percents based on the total weight of the blowing agent):

- (1) CFC-12, CFC-124, CFC-134A, CFC-142B, CFC-143A and mixtures thereof;
- (2) Any of the CFCs of 1 in a mixture with up to 6 percent CO2;
- (3) 55 to 97 percent EtCl and 3 to 45 percent CO2;
- (4) The blowing agent of (3) in a mixture with up to 90 percent of a CFC selected from CFC-12. CFC-142B and mixtures thereof;
- (5) 19 to 97 percent EtCl and 3 to 81 percent CO2;
- (6) The blowing agent of (5) in a mixture with up to 90 percent of a CFC selected from CFC-12. CFC-142B or mixtures thereof;
- (7) The blowing agent of (3) in a mixture with up to 90 percent of a mixture of CFC-12 and one or more CFCs selected from CFC-134A, CFC-124 and CFC-143A;
- (8) The blowing agent of (5) in a mixture with up to 90 percent of a mixture of CFC-12 and one or more CFCs selected from CFC-134A, CFC-124 and CFC-143A;
  - (9) 20 to 97 percent EtCl and 3 to 80 percent of CFC-12, CFC-142B. CFC-134A. CFC-124, CFC-143A and mixtures thereof;
  - (10) The blowing agent of (9) in a mixture with up to 3 percent CO<sub>2</sub>;
- (11) The blowing agent of (1) in a mixture with up to 40 percent of CFC-22;
  - (12) The blowing agent of (11) in a mixture with up to 5.5 percent CO2;
  - (13) The blowing agent of (1) in a mixture with up to 50 percent ethane:
  - (14) The blowing agent of (13) in a mixture with up to 6 percent CO2;
  - (15) The blowing agent of (1) in a mixture with up to 50 percent propane;
- (16) The blowing agent of (15) in a mixture with up to 6 percent CO2;
- (17) The blowing agent of (5) in a mixture with up to 90 percent of the blowing agent of (1), and up to 50 percent ethane;
- (18) The blowing agent of (5) in a mixture with up to 90 percent of the blowing agent of (1), and up to 50 percent propane;

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- (19) The blowing agent of (5) in a mixture with up to 90 percent of the blowing agent of (1), and up to 50 percent of CFC-22;
  - (20) CFC-22;

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- (21) The blowing agent of (20) in a mixture with up to 5 percent CO<sub>2</sub>;
- (22) The blowing agent of (20) in a mixture with up to 50 percent ethane:
- (23) The blowing agent of (21) in a mixture with up to 50 percent ethane:
  - (24) The blowing agent of (20) in a mixture with up to 50 percent propane;
  - (25) The blowing agent of (21) in a mixture with up to 50 percent propane;
  - (26) EtCl and up to 40 percent CO2;
  - (27) EtCl and up to 70 percent ethane;
- (28) The blowing agent of (26) in a mixture with up to 70 percent ethane:
  - (29) EtCl and up to 70 percent propane:
  - (30) The blowing agent of (26) in a mixture with up to 70 percent propane:
  - (31) EtCl and up to 70 percent CFC-22;
  - (32) The blowing agent of (26) in a mixture with up to 70 percent CFC-22:
- (33) The blowing agent of (31) in a mixture with up to 70 percent ethane:
  - (34) The blowing agent of (31) in a mixture with up to 70 percent propane:
  - (35) H<sub>2</sub>O:

synthetic resin into an extruder where the resin is heat-plasitifed.

The heat-plastified resin is then passed through a pressure control device, such as a gear pump. The pressure control device controls the discharge pressure of the extruder and more importantly the inlet pressure to the mixing device, such as a rotary pin mixer.

The blowing agent is introduced into the rotary pin mixer and the desired pressure is obtained by adjusting the pressure control device and the temperature of the mixing device.

The discharge from the mixing device is then passed through a cooling device, such as one or more heat exchangers of the variety shown in U.S. Patent No. 3,014,702.

The discharge from the cooling device is then passed through the die and expanded. The foam examples in this specification are expanded at atmospheric pressure; however, the foam expansion could also occur in subatmospheric pressure.

By maintaining a constant die inlet pressure and adjusting the pressure drop from the mixer's inlet to the die's inlet over a range of pressure drops such that the quality of the extruded foam's surface changes form poor to good (or vice versa), a "critical minimum pressure drop",  $\Delta P_C$ , for a given blowing agent can be determined. This critical pressure drop depends on the blowing agent and alkenyl aromatic synthetic resin combination and is easily determined by simple experimentation which consists of holding the die pressure constant while adjusting the mixing device pressure until extruded foam having a good skin and no blow holes is produced with no gassing at the die.

The critical pressure drop is then determined at that point and is the difference between the mixing device pressure and the die pressure.

Knowing the critical pressure drop, which is for a given blowing agent and alkenyl aromatic synthetic resin, the die pressure, which must be greater than atmospheric pressure, can be adjusted. However, that die pressure plus the critical pressure drop for that blowing agent must also be greater than the vapor pressure of the blowing agent and is the minimum pressure which must be maintained in the mixing device in order to produce extruded foam having a good skin, virtually no blow holes and little or no gassing at the die.

Restated simply, the sum of the die pressure and the empirically determined critical pressure drop, is the minimum mixing pressure at which the mixing device must be maintained to produce quality extruded alkenyl aromatic synthetic resin foam.

The mixing device must be operated at least at the critical mixing pressure and can also be operated above the critical mixing pressure.

This requirement of a minimum operating pressure in the mixing device is not method, process or system dependent; the numerical value of the minimum acceptable operating pressure in the mixing device is primarily dependent on the blowing agent used and much less dependent on the specific extrusion process (such as those shown in Figures 1-19) as well as the precise location of pressure guages etc. Accordingly, this invention applies to any extrusion method for producing alkenyl aromatic synthetic resin foam.

The following examples illustrate ways in which the principle of the invention has been applied; but should not be construed as limiting the invention.

Foams were prepared from several different polymers, a large number of different blowing agents, using apparatus shown schematically in Figure 3. In particular, essentially, a 1½ inch (3.8cm) extruder was used in combination with a ½ horsepower (370W) gear pump manufactured by Zenith; a mixer of the rotary pin type disclosed in U.S. Patent No. 3,770,668; flat plate coolers of the type shown in U.S. Patent 3,014,702; and a slit extrusion die having an adjustable gap. The polymer throughput rate was 10 pounds (4.5kg) per hour.

Tables 1-5 show the processing conditions and some of the product properties, as well as the empirically determined values of critical pressure drop, ΔP<sub>C</sub>, for each of the exemplified combinations of polymer and blowing agents.

The following abbreviations are employed in this specification, including the drawings:

PS	polystyrene having a weight average molecular weight of about 200,000 as meas	urea by
	the gel permeation chromatograph method	

SAA	styrene/acrylic acid copolymer having a weight average molecular weight of about 165.000
	as measured by the gel permeation chromatograph method

CISAA calcium ionomer of SA	ď
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BA	blowing agent
pph	parts per hundred
`F	degrees Fahrenheit
RPM	revolutions per minute

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	Quality	Surface	Good	Puor Good	Good	Good Good Fair Poor	Good	Poor Good	Puor Good	Good
	1531VE 11 (psu)	01		765	32.1		12 8		49.3	
	Compressive Strength (pst)	MD		11.5	36.0		435		12.6	! !
$\sim$	Foam	(ww)	0.1	1.2	0.59	0 1 0 0 1	0 59		0 90	0 22 0 26
FOAM	form	(pct)	2.46	309	2.42	233 237 227 239	2.19		2 64	1.82
LONG-TERM INSULATING BLOWING AGENTS FOR POLYSTYRENE FOAMS	ΔP <sub>C</sub> Critical Pressure	Drop (psi)	440	370	150	460	320	480	200	270
OR POLY	PMC	(psd)	01.810	1020	1190	1660	1520	1450	1430	1180
GENTS F	P., Die	sure (psr)	0601 V 0601	050	840	1210. 1210. 1210. 1210.	1200	970	850 050	910
WING A	Imise	S	158	180	156	155 159 166 175	. 160 -	159	178	152
ING BIL	Pm Mine! Inlet	Pres Sure (px)	1550	0001	1,100	1750 1690 1650 1610	1320	1430	0/61	0171
NSULAT	Mixer	RPM	01	0.	0.	2 , , ,	5 '	0.	2 .	<u>o</u> ,
TERM !	foam	(4) 1.	061	6.	e.	0	0.1	oc	35.	5. ·
	lutal BA	(pph)	14.4	611.5	130	6	101	6 01	= .	0 ~ .
Table 1	illuwing Agent Systems	(Components in pph)	0.00	(IC.142B	6 SCIC 12/	10 B G G C - 12/	9 UCI C-1420/ 1 1 CO)	CI C 142B/CFC-12/CO,	CIC 22/CO <sub>2</sub> /CFC-12	C1C 22/CO/C1C 142U
		Type	۶.	₹.	ž.	z	₹.	۶.	₹.	ε.
	t and the	2 2	₹ 9	₹ ₹	<u> </u>	4 # 4 6	\$ #	499	₹ ₹	80

	_			44.54 Is	<del></del>		a		1.	1·	
_		Quality	Surface	Guod	Poor	Poor Good	Poor	Good	Pour	Pour	Good
5		h (pst)	2		12.4			10.1	42.9 47.9	10 th	
10	·.	Sucanjaco) Sucanjak	: : OW		70.5	: :		76.1	10 5 9 9	16.8	:
	s w s	fount	(mm)	0.20	0 50 0 50	0 46 0 50	0.96	901	177	7 7 7 1 62	0 31
15	ONG-TERM INSULATING BLOWING AGENTS FOR POLYSTYRENE FOAMS (CONTINUED)	foam Density	(pr.f)	1.77 .	181	1 79	2.00	171	2.03	2.13	1 96
	LYSTYRI	AP. Critical Press	Sure Drop (pst)	790	780	270	300	750	06.7	410	455
20	FOR PO	Pat Control Pres	Sure (pst)	0601	1160	1170	1620	1050	0000	1700	15.25
	GENIS	P., P.	Sure (psi)	008	080	006	720	ຄດຄ	590 590	790 790	1070
25	(CONTINUED)	<sup>1</sup> дине (°С)		154	179 165	178	169 159	154	154 156	17.9	15.7
	16 BLOV	P <sub>ri</sub> Mixer Intet	Sure (Frs.)	1120	0511	0911	1000	0801 0801	070	1140	1540
30	IUI ATIN	Mine	S .	o .	91 ,	2 ,	2 ,	0.	2,	5 '	2 .
35	RM INS			δ.	e,	e.	08.	130	97.	130	0.1
	ONG-TE	lotal	(pph)	=:	7:	2.	2 01	10.4	0	î a	8 .
40	ABIL 1	Systems	(gdd m	5	=	77 313	יויל אוי.	3117 7/112	27-313MH		
		uluwung Agent Systems	(Components in pph)	1 5/1 3/6 0/0 25	1 511 316 0/0 37	13/13/60/01/01/01/02/22	11CHCO,/CFC-142HK, 111.	1101/CO,/CLC142/U/C, 1/18, 2 5/1 3/6 0/0 6	110 W O JOH C   147 WOLL C 22	11,01/CO,1/C1C,142B	11,0/CO,/CIC 12
45	**	Blow	:	וניגנס	1511 34	לינינעכטיענוכ זיניוענטיענוכן	11000	1	וינוע ס'ענו	1 9/1 3/6 0	
		Poly.	lype I	€.	ξ.	€ .	₹.	€,	€.	€.	<u>ē</u>
50		Luample	N O	14A 14B	15A 15B	191	1/A 1/6	18A	AC1	20A ; 20U	717 V17

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5		Compressive Strength (KPa)		1 1	1 1	1 1		
70					X			private to the second
15		Foam Density (kg/m³)	35.2	36.0	32.5 29.8	34.3	35.2	
20	valents	A PC Critical Pressure Drop (MPa)	3.2	3.4	2.3	2.7	3.7	
25	Metric Equivalents (Continued)	PNC Critical Pressure (MPa)	9.4	6.6	9.7	10.1	12.6	
30	Table 1	PD Die inlet Pressure (MPa)	6.2	6.5	7.4	7.4	0.6	
35 40		PM Mixer inlet Pressure (MPa)	9. 6	9.8	10.0	10.3	12.8	
45	The same of all and a second of the second o	Foam Temp TF (°C)	54	54	54	54	5.4	
50		Example No.	9.A 9.B	10A 10B	11A 11B	12A 12B	13A 13B	

TABLE 2 LONG TERM INSULATING BLOWING AGENTS FOR SAA (97/3) COPOLYMER FOAMS

nemple	Polymer Lype		lotal BA:	Foam	Мінез	P.M. (Mixel Indet	] Mirei	ud oid oidi	PML Catical Pres	ΔΡ <sub>L</sub> Critical Pres-	foam Density	Foam	Compressive Strength (pst)	Cumpressive Strength (pxt)	Quality of Foam
§		(Components in pub)	(bbp)	£.	ž Ž	sure (pst)	3	sure (psi)	(lss)	Drop (psr)	( <del>)</del>	(mm)	MD	Q1	Surface
22A 22B 22C	SAA (37AA)	CFC-12/CO, 11 6/1 0	126	0.	2 , ,	1640 1730 2040	182 169 164	1110	0691	980	250 257 257	77 O 11 O		75.4	Puor Good - trickent
230 230 230 210	SAA (1%AA) CFC-1420	CFC-1420		0	2	1170	921 171 971	7.0 0.77 1000°	9111	340	2 84 3 18 2 99 2 84	97 0	1:17	5.73 5.73 5.53	Good Good Foor Good
24A 24U	SAA (1%AA) CFC-1428/CO,	CFC-1420/CO, 9 //1 0,	10.7	130	0.	1230	180	006	0671	390	2 70	0 81	26.0	59.0	Poor
25A 25B	SAA (35.AA)	CFC-1420/C1C-12 6 5/6 5	130	0[.	01 -	1320	164 168	0/6	1290	320	2.26 2.20	01 0 01 0			Good
26A 268	SAA (3::AA)	SAA (3%AA)   CFC-142BKO,KFC-12   5 311 0/5 3	116	130	o: .	1290	191	910	12904	380	2.74	0 J1 0 24 0	: :	5/4 5/8	Good

\* Pressure was increased by decreasing the die gap.

_						
5	Compressive Strength (kPa) MD 'TD	- 520 - 531 - 462	- 435 - 357 - 395 - 383	248 407 194 425		- 36 (133) 6.
15	Foam Density (kg/m³)	41.2	45.5 50.9 47.9 45.5	43.2	36.2 36.5	43.9
o valents	A PC Critical Pressure Drop (MPa)	4.0	2.3	2.7	2.2	2.6
Metric Equivalents	PMC Critical Pressure (MPa)	11.7	7.7	6.8	8.9	6.8
8 Table 2	PD Die inlet Pressure (MPa)	7.7 7.7 10.0	5.3 5.3 6.9	6.2	6.7	6.3
40	PM Mixer Inlet Pressure (MPa)	11.3 11.9 14.1	8.1 7.7 7.5 9.7	8.5 9.3	9.1	8.9 8.6
45	Foam Temp TF (°C)	5.4 5.4 5.4	54 54 54	54	λ. ν.	54
5 <b>0</b> .	Example No.	22A 22B 22C	23A 23B 23C 23D	24A 24B	25A	26A 26B

TABLE 3 LONG TERM INSTITUTING BLOWING AGENTS FOR CISAA (97/3) COPOLYMER FOAMS	
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NO. NO.	Polymer Type	Blowing Agent Systems (Companents in plib)	Fotal BA Level (pph)	Foam Temp T, (°F)	Mixe	PM Minet Inlet Pres- sure (psi)	T Miles	PD Die Pres. Sure (ps.)	Pac Cintral	APr. Citical Pres. Sure Drop (psi)	Froam Density (pcD)	Foam Cell Size (mm)	Compressive Strangth (pss)	h (pss)	Quality of Foam Surface
32A :	5AA (37;AA) 1	CFC 124CO,	126	DC .	0.	1610	183	1180	1700	\$20	2.64;	01.0	1 1	60%	Poor
33A 138		CfC-1428	611	0	01	0501	169:	750	0101	260	.212:	0 16		397	Good
14A 140		CFC.142U/CO, 9.7/1.0	10.7	071	10	1320	168	000	1350	490	2.75 2.86: 2.62	011	 	\$5.2 60.9 75.2	PODT GOOD
350 350 350		CFC-12/CFC 142B 6 5/6 5	13.0	oc. ,	9,	1200	178	020 020 1220	0111	490	2.78 2.73 2.73	100 110 110	!!:	637	Poor Fair Good
76A 164		CFC-1421HCO.jR.1 C-12 4 911 114 9	6 01	06.1	2 ,	2240	161	1660	0077	\$20	2.05	110	: :		Good
17.4		CIC-121/0/1/1/C 12 4 JN 3/10	ē.	š.	o.	1950	07.1 27.1	1450	0 < 0.1	200	2.54	0 0	: ;		Good
780		CEC-22/CO <sub>2</sub> /CIC 142B 3 70: 307 0	12.0	g .	2	1570	180	0011	07.91	330	7.75	2 2 2	: :		Four

\*Pressure was increased by decreasing the die gap.

10	
15	
20	9 4 0 0 1 0 1 0
25	
30	:
35	
40	

	Streng (kp	489	_ 299	- 381 - 420 - 519	1. 1.	1 1		1 1
	Foan Density (kg/m³)	42.3	34.0	44.1 45.8 42.0	44.5 43.7 44.7	33.0	40.7	36.2
valents	∆PC Critical Pressure Drop (MPa)	3.6	1.8	3.4	3.4	3.6	3.4	2.3
Metric Equivalents	PhC Critical Pressure (MPa)	11.7	7.0	6.3	0.6	15.2	13.4	11.2.
Table 3	PD Die inlet Pressure (MPa)	8.1 8.1	5.2	5.9	5.7 5.7 8.4	11.6	10.0	0.6
	PM Mixer inlet Pressure (MPa)	11.11	7.2	9.1 9.5 10.8	8.3 8.7 11.9	15.4	13.4	10.8 11.2
	Foam Temp TF	54	54	54 54	54	5.4	54 :	54
	Example No.	32A 32B	33A 33B	34A 34B 34C	35A 35B 35C	36A 36B	37A 37B	38A 38B

TABLE 4 NON-LONG-TERM INSULATING BLOWING AGENTS FOR POLYSTYRENE FOAMS
AGENTS
BLOWING
INSULATING
NON-LONG-TERM
TABLE 4

Quality of Foam	Sufface	Good	Good	Poor Good	Good	Poor	Poor	Good
assiva h (psi)	gu ,		4/3	49.2 52.8	72.8		: :	58.4
Compressive Strength (pst)	MC	1 1	24.2	10 S. 9 7	13.2	: :	: :	6.3
foam	(min)	0.13	0.28	2.71 3.24	2.79	3 35 2 80	1 58 2.86	2.72
form	(pct)	1.90	1.86	2.05 2.08	2.41 2.18	1.95	2.29	2.23 2 19
AP., Catacal Pres-	Sure Drop (psi)	350	340	280	330	300	330	310
P <sub>IAL</sub> Cutical Pres-	Sure (psi)	1380	1230	940	1030	1070	0101	900
P <sub>II</sub> One	yure (psr)	1030	068	099 099	700	077 077	680 680	590 590
I Miner	S ::	155	153	174 165	155	180	177	153
P.M. Miner Miner	Pres.	1400	1250	930	1060	1040	990	920 890
Mires	M M	0.	0.	0,	9;	٥,	2,	2,
Foam	(£) '1	130	130	130	06.	130	130	130
Potal	t evel (pph)	1.0.1	9.2	6.5	6.9	9.6	94	9.8
Blowing Agent Systems	(Components in pph)	CFC-22/CO,/C,H,	CFC-22/CO,/C,11 <sub>8</sub> 6 0/1 3/1 9	E1d/CO,/C,11,	E1CI/CO,/C,H, 3.5/0.9/2.5	ELCI/CO,/CFC-22 3.5/1.3/5.0	E1CI/CFC-22/C,H, 3.5/5 0/0.9	E1CI/CFC-22/C,H <sub>6</sub> 3.5/5.0/1.3
Polymer		S.	۶.	PS .	PS :	Şđ.	8.	PS.
t nample	0	44A 44B	45A 45B	46A 46B	47A 47B	48A 48B	49A 49B	50A 500

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Compressive Strength (kPa) MD TTD		167 326	72 339 67 12(364	91 502 108 430		1 t	50 413 43 403
Foam Density (kg/m³)	30.4	29.8	32.8	38.6	31.2	36.7 35.7	35.7
A PC Critical Pressure Drop (MPa)	2.4	2.3	1.9	2.3	2.1	. 2.3	2.1
PMC Critical Pressure (MPa)	9.5	8.5	6.5	7.1	7.4	7.0	6.2
PD Die inlet Pressure (MPa)	7.1	6.1	4.6	4.8	5.3	4.7	4.1
PM Mixer inlet Prossure (MPa)	9.7	8.6	6.4	7.3	7.2	6.8	6.3
Foam Temp	54	54	54	54	54	54	54
Example No.	44A 44B	45A 45B	46A 46B	47A 47B	48B	49A 49B	50Å 50B

foregoing is intended to be merely illustrative and is not to be construed or interpreted as being restrictive or otherwise limiting of the present invention, excepting as it is set forth and defined in the hereto-appended claims.

A COPOLYMER FOAMS
ING AGENTS FOR SAA AND CISAA COPO
AGENTS FO
NG BLOWING
IM INSULATI
ABLES NON-LONG-TERM INSULATING BLOWING AGE
TABLE S

1 12 0 19			· ·			<del></del>
Quality of Foam	Surface	Good	Good	Poor Good	Poor	Good
essive li (psi)	T. CI	40.1		30 6	39.1	49.5 36.9
Compressive Strength (pst)	M		: :	12.5		73.1
fear Cest	(mm)	0.32	0.38	3.25	0.93	0.24
form Density	(prt)	2.72	2.47	2.53	2 2 1 2 18	3.16
ΔP <sub>C</sub> Critical Pres-	Sure Drop (px)	400	370	510	430	630
Pac Critical Pres	sure (psd)	1340	1520	1570	1790	1480
P <sub>D</sub> Die mlet	Pies.	940	1150	1060	1360	850 850
I Muser	ુ .	164	165 168	180	180	991
P.M. Mixei Inlet	Pres. Sure (psv)	1360	1560	1560	1710	1570
Miner	M de	0.	2,	2,	2,	0.
<b></b>	€.	130	130	130	130	130
lutal	(pph)	6.5	4 8	0.9	8 75	6.5
Blowing Agent Systems	(Components in 1941)	EICI/CO,/C,II,	H,O/CO,/C,N <sub>a</sub>	11,0/CO,/E1Cl 0 971.3/3.7	SAA (3%,AA) 11,0/C0,/CFC-22	E1CI/CO,/C,11, 3.5/1.3/1.7
	Polymer Type	SAA(3%AA) EICHCO,/C,H.	SAA (3%AA)	SAA (3%6AA) 11,0/CO,/E1CI	SAA (3%AA)	SAA (3%AA) ELCI/CO,/C,11, 0.5 pph 3.5/1.3/1.7 Ca(O11),
f nothly		54A 54B	55A 558	56A 568	57A 57B	SUA SUB

	_								
5	er see	Compressive Strength (kPa) nD TD	276		211 246	270 219	341	2.000 TO	474 288 308
10		Comp. S.L.	1 1	-1 1	8E1	15 1	504		340 228 345
15		Foam Density (kg/m³)	43.6	39.6	40.5	35.4	50.6 46.6	40.8	44.1
20	Equivalents	L PC: Critical Pressure Drop (MPa)	2.8	2.6	3.5	3.0	4.3	2:4	3.4
25	Metric Egu	PMC Critical Pressure (MPa)	9.2	10.5	10.8	12.3	10.2	9.4	8.4
30	Table 5	PD Die inlet Pressure (MPa)	6.5	7.9	7.3	9.4	5.9	7.0	7.6
40		PM Mixer inlet Pressure (MPa)	9.4	10.8 10.2	10.8	11.8 13.0	10.8	9.6	11.0
45		Foam Temp Tr (°C)	54	54	54	54	54	54	5.4 5.4 5.4
50		Example No.	54A 54B	55A 55B	56A 56B	57A 57B	58A : 58B	59A 59B	60A 60B 60C

#### 55 Claims

#### EP 0 445 847 A2

- (22) A blowing agent of (20) including up to 50 percent ethane:
- (23) A blowing agent of (21) including up to 50 percent ethane:
- (24) A blowing agent of (20) including up to 50 percent propane:
- (25) A blowing agent of (21) including up to 50 percent propane:
- (26) 20 to 90 percent EtCl and up to 40 percent CO2;
- (27) 20 to 90 percent EtCl and up to 70 percent ethane;
- (28) A blowing agent of (26) including up to 70 percent ethane;
- (29) 20 to 90 percent EtCl and up to 70 percent propane;
- (30) A blowing agent of (26) including up to 70 percent propane:
- (31) 20 to 90 percent EtCl and up to 70 percent CFC-22;
  - (32) A blowing agent of (26) including up to 70 percent CFC-22;
  - (33) A blowing agent of (31) including up to 70 percent ethane:
  - (34) A blowing agent of (31) including up to 70 percent propane;
  - (35) H<sub>2</sub>O;

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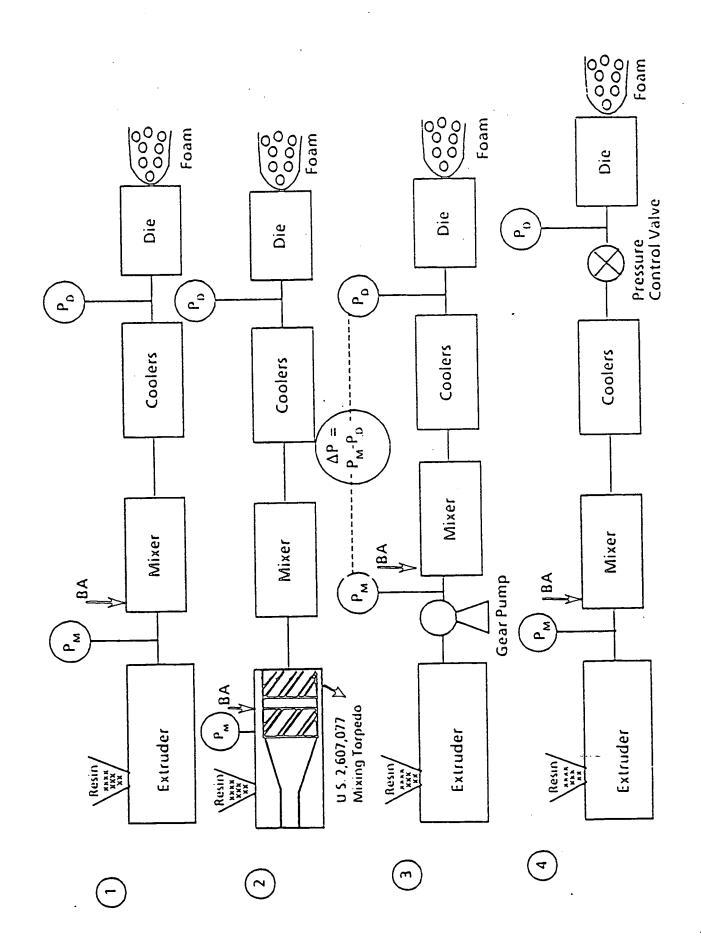
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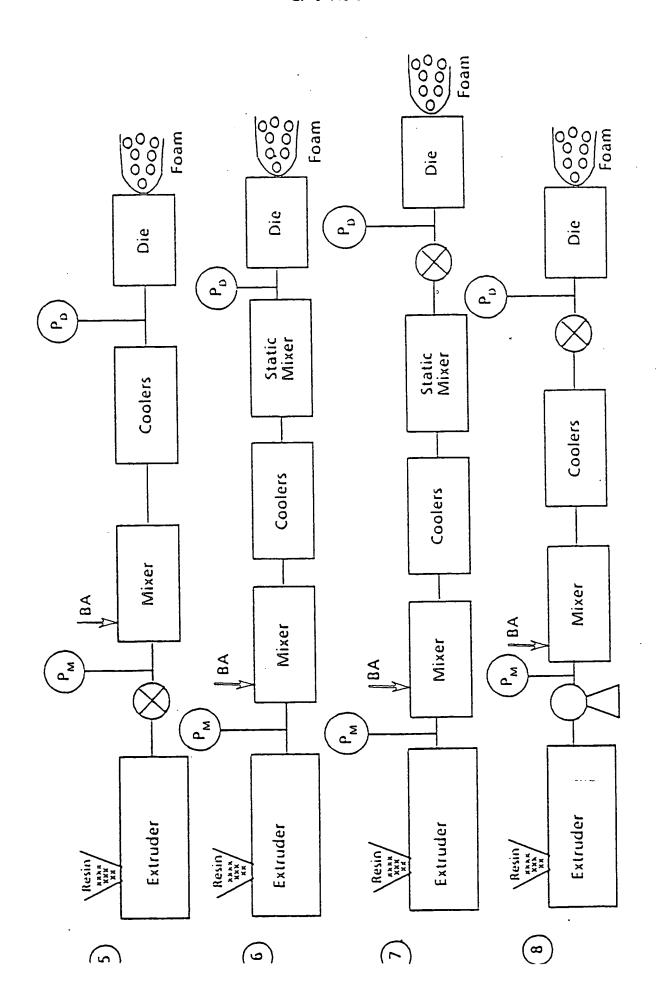
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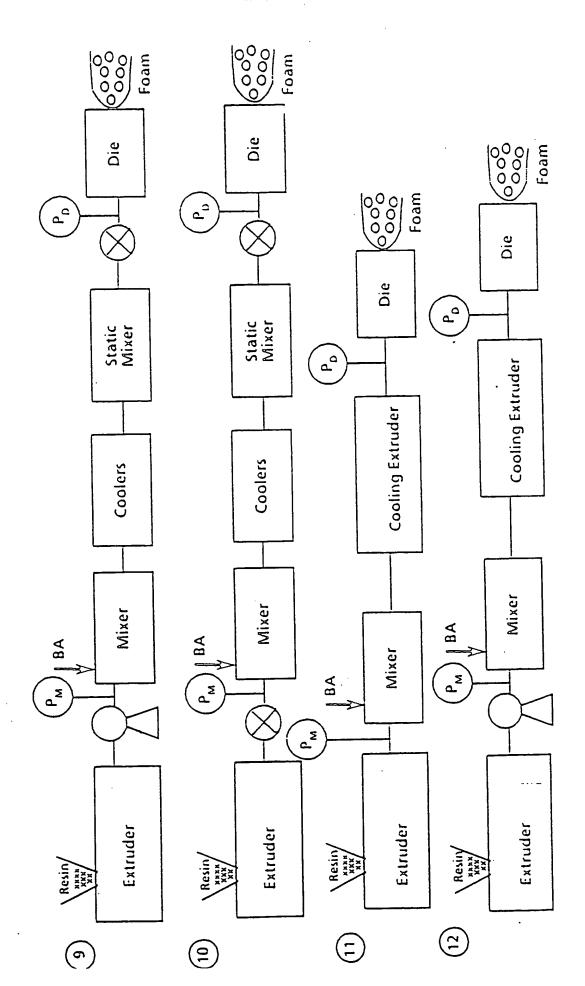
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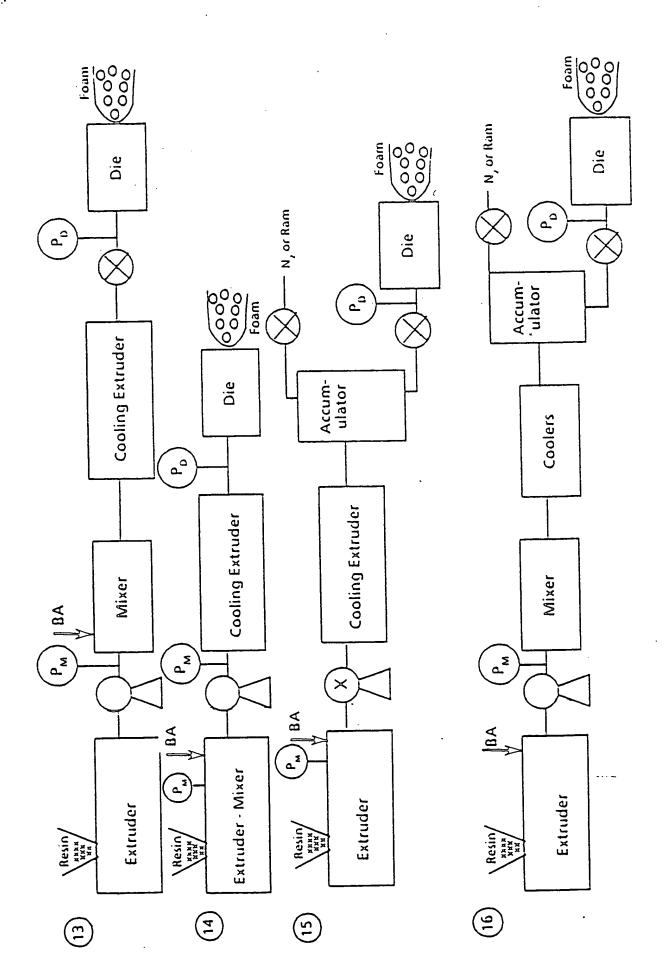
- (36) 0.4 percent to 99.9 percent H2O and 0.1 percent to 50 percent CO2;
- (37) A blowing agent of (36) including up to 99.5 percent of the blowing agent of (1);
- (38) 0.4 to 99.9 percent H<sub>2</sub>O and up to 60 percent CFC-22;
- (39) A blowing agent of (36) including up to 60 percent CFC-22;
- (40) A blowing agent of (38) including up to 60 percent of ethane, propane, EtCl or mixtures thereof;
- (41) 0.4 to 99.9 percent H<sub>2</sub>O and up to 60 percent ethane;
  - (42) A blowing agent of (36) including up to 60 percent ethane;
  - (43) 0.4 to 99.9 percent H<sub>2</sub>O and up to 60 percent propane;
  - (44) A blowing agent of (36) including up to 60 percent propane;
  - (45) 0.4 to 99.9 percent H<sub>2</sub>O and up to 60 percent EtCl; and
- (46) A blowing agent of (36) including up to 60 percent EtCl.
- 4. A method as claimed in any one of the preceding claims wherein the resin is polystyrene.
- 5. A method as claimed in any one of Claims 1, 2 and 3, wherein the resin is a styrene/ acrylic acid copolymer having one tenth (0.1) weight percent to fifteen (15) weight percent polymerized acrylic acid by total resin weight.
  - 6. A method as claimed in any one of Claims 1, 2, 3 and 5, wherein the resin is an ionomeric styrene/acrylic acid copolymer.
  - 7. A method as claimed in Claim 6, wherein the ion is selected from calcium, sodium, lithium, potassium, magnesium and mixtures of these ions.
- 8. A method as claimed in Claim 7, wherein the ions for the ionomeric styrene acrylic acid copolymer are provided by addition to the heat plastified resin in step (a) of one tenth (0.1) to one (1) parts per hundred by weight per hundred parts by weight of resin of a neutralizing agent selected from calcium hydroxide, lithium hydroxide, sodium hydroxide, potassium hydroxide, magnesium oxide and mixtures of these compounds.
- 45 9. A method as claimed in Claim 8, wherein said amount of neutralizing agent added is one tenth (0.1) to six tenths (0.6) parts per hundred by weight per hundred parts by weight of resin.
  - 10. A method as claimed in any one of the preceding claims further comprising the step of passing the plastified resin through a pressure control device, after step (a) and before step (b).
  - 11. A method as claimed in any one of the preceding claims, wherein a drop in the value of  $\Delta P$  is corrected by
    - (a) reducing the temperature of the mixing device:
    - (b) partially closing a throttle valve located between the mixing device and the die's inlet:
- 55 (c) reducing the blowing agent concentration; and/or
  - (d) increasing the feed rate of the resin into the mixing device.
  - 40. A method as claimed in any one of the preceding claims wherein the value of  $\Delta P$  is continuously





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